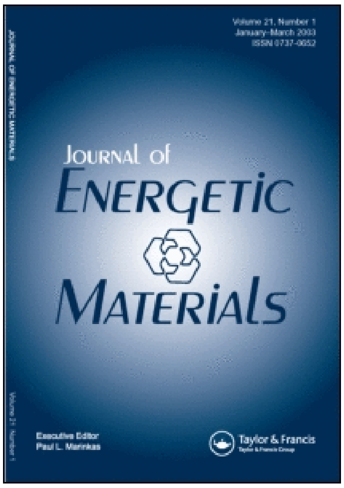

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Control of the Particle Size of Submicron HMX Explosive by Spraying in Non-Solvent

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Preparation and characterization of cyclotetramethylene tetranitramine (HMX; octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine) submicron particles by spraying in non-solvent technology at different process parameters was investigated in this article. The results indicated that the process parameters, such as addition of surfactant, slurry, and anti-solvent temperatures; compressed air flow rate; slurry flow rate; stirring the anti-solvent; and nozzle diameter played important roles in controlling the performance of HMX submicron particles, such as particle size, size distribution, etc. The produced HMX particles by spraying in a non-solvent method were identified and characterized by X-ray powder diffraction (XRD) and scanning electron microscopy (SEM). The results showed that this method is simple for micronization of energetic materials and would be an effective method for large-scale preparation of submicron particles of HMX explosive. Finally, the optimum condition for the preparation of fine powder of HMX by spraying in a non-solvent method was proposed.

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Keywords: micronization of explosive, parameter optimization, particle size control, spraying in non-solvent process, submicron HMX

Introduction

The preparation of micro- and nano-structured energetic materials has recently drawn considerable attention as a potential method that can be used to obtain energy release more rapidly than conventional materials. Very fine particles of materials in fact exhibit properties significantly different from those of the same material with large sizes [1]. In the case of solid explosives and propellants, small particles are required to improve the combustion process. Indeed, the maximum energy output from a detonation the particle size of material [2].

Several techniques have been used for manufacturing very fine particles, such as grinding, crystallization, spray freezing into liquid nitrogen, wet and jet milling, spray drying, and supercritical fluid [3–7], but these techniques suffer from inherent limitations. The major disadvantage of these techniques is high temperature to evaporate the solvent, difficulty controlling particle size and particle size distribution, and limitations for industrial manufacturing and safety processing. We report the preparation of submicron cyclotetramethylene tetranitramine (HMX; octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine) by the spray solution of HMX into water as a non-solvent, which is a novel process developed to produce submicron particles.

The sensitivity and the performance change significantly when the size of the energetic materials is reduced to submicron scale.

Particles are formed by atomization of an acetone feed solution containing the HMX into water. This method is a very safe and reliable technique [8].

HMX is a high explosive used in many plastic-bonded explosives (PBX), double base propellants, and propellant composites because of its high calorific potential, high density, and smokeless combustion products [9,10].

Preparation of nanoscale high explosive (HE) materials like pentaerythritol tetranitrate (PETN) and HMX has been a challenging task, due to their chemical and physical properties such as decomposition at relatively low temperatures. HMX ($C_4H_8N_8O_8$) is used almost exclusively in military applications and also as a propellant. It has also been the subject of various fundamental studies [11–15]. Although these materials have been studied at the macroscopic level, very little is known about their behavior at the nanoscale. Engineering and control of energetic material properties at the nanoscale are of paramount importance when the ignition and detonation properties of HE are to be determined.

The main purpose this study was to prepare of submicron HMX and investigate the effect of various process parameters such as slurry concentration, solvent and anti-solvent temperature, etc., on the particle size of HMX and its distribution.

Experimental

Sample Preparation

Submicron samples of HMX were produced via spraying in non-solvent technique in acetone solvent and water as anti-solvent. In this technique, 30 g of pure crystalline HMX with 50 µm average particle size was dissolved in 1000 mL of acetone. Submicron particles were obtained by spraying in non-solvent using a mini spray nozzle LPH80 equipped with a 0.8-mm-diameter two-fluid nozzle, which operates in a cocurrent mode. Various samples of HMX with different particle sizes were obtained by performing spraying in non-solvent experiments at various conditions according Table 1.

HMX Particles Characterization

Scanning electron micrographs were recorded using a Philips XL30 series instrument using a gold film for loading the dried particles on the instrument. Gold films were prepared by a sputter coater model SCD005 made by BAL-TEC (Switzerland). The structure and morphology of the HMX were examined by means of X-ray diffraction (XRD, Thermo X'TRA, Cu Kα radiation).

Table 1
The processing parameters for spraying in non-solvent of HMX explosive

No.	Isopropyl alcohol addition	Solvent temp. (°C)	Compressed air flow rate (L/min)	Slurry flow rate (L/min)	Anti solvent temp. (°C)	Avg. particle size (µm)
1	−	20	20	0.0025	0	14.98 (±0.2)
2	+	20	20	0.0025	0	0.617 (±0.234)
3	+	50	20	0.0025	0	0.647 (±0.223)
4	+	20	40	0.0025	0	0.347 (±0.141)
5	+	20	40	0.0075	0	0.481 (±0.2)
6	+	20	40	0.012	0	2.377 (±0.736)
7	+	20	40	0.0025	20	11.97 (±3.125)

Results and Discussion

HMX exists in four solid-phase polymorphs, labeled α, β, γ, and δ-HMX [16,17], each of which can reportedly be prepared by a specific cooling rate of a reaction solution [18]. The β phase of HMX has the highest density and is stable at room temperature; it is the form in which HMX is normally produced and used. However, when heated to temperatures above 162°C, the β phase converts to the δ phase HMX [16,19–22]. Figures 1 and 2 show the XRD patterns related to the β and δ phase HMX, respectively.

Effect of Addition of Surfactant on Particle Size

Control of the particle size can be achieved by adding surfactants to vary the interfacial forces. Figure 3 shows the influence of surfactant on the particle size of the prepared HMX particles. When isopropyl alcohol is added to the anti-solvent, the stability of the droplet decreases and the size of the prepared particles is decreased. The effect of the addition of isopropyl alcohol as the interfacial forces reductant on the particle size of the prepared HMX particles is shown in Fig. 3. The size of

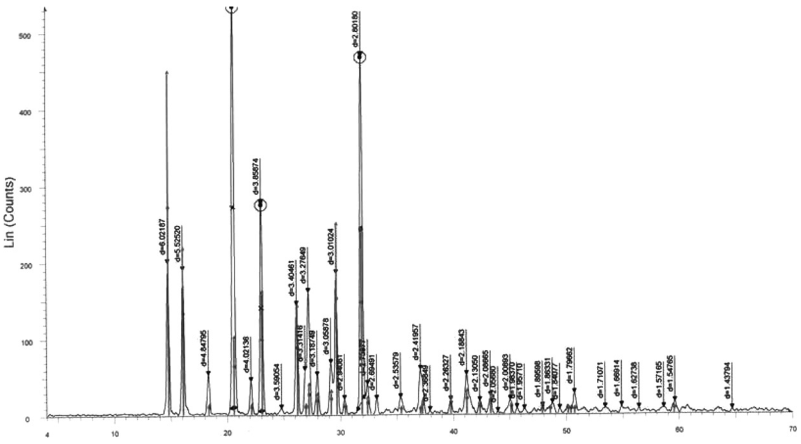


Figure 1. XRD pattern of β-HMX.

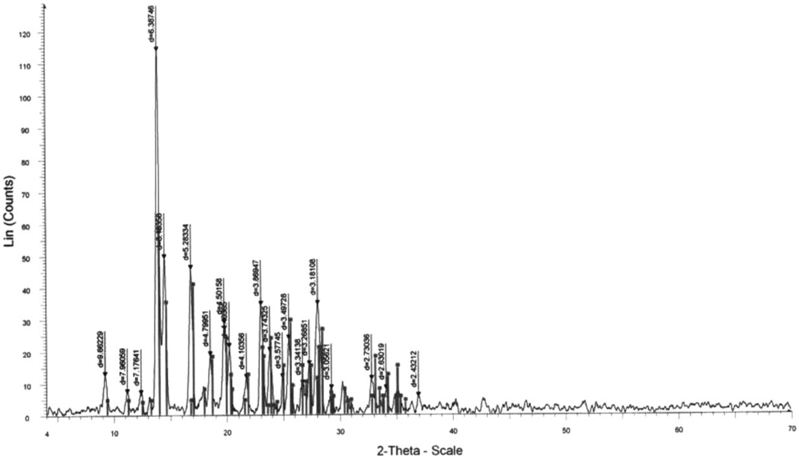
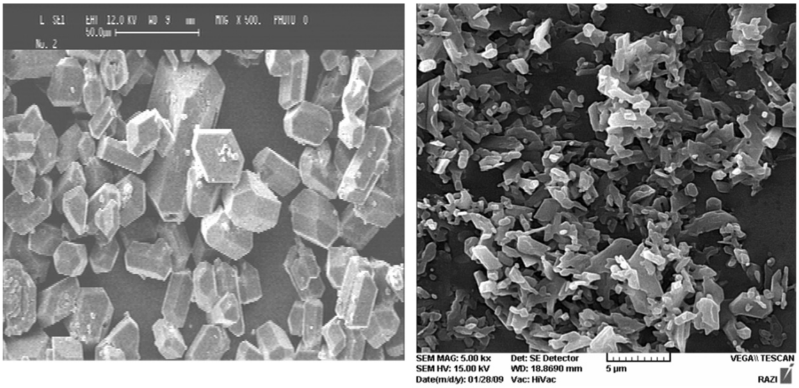


Figure 2. XRD pattern of γ-HMX.

produced HMX particles in the presence of isopropyl alcohol was 617 nm and in the absence of isopropyl alcohol as reductant of interfacial forces was 14.98 µm.

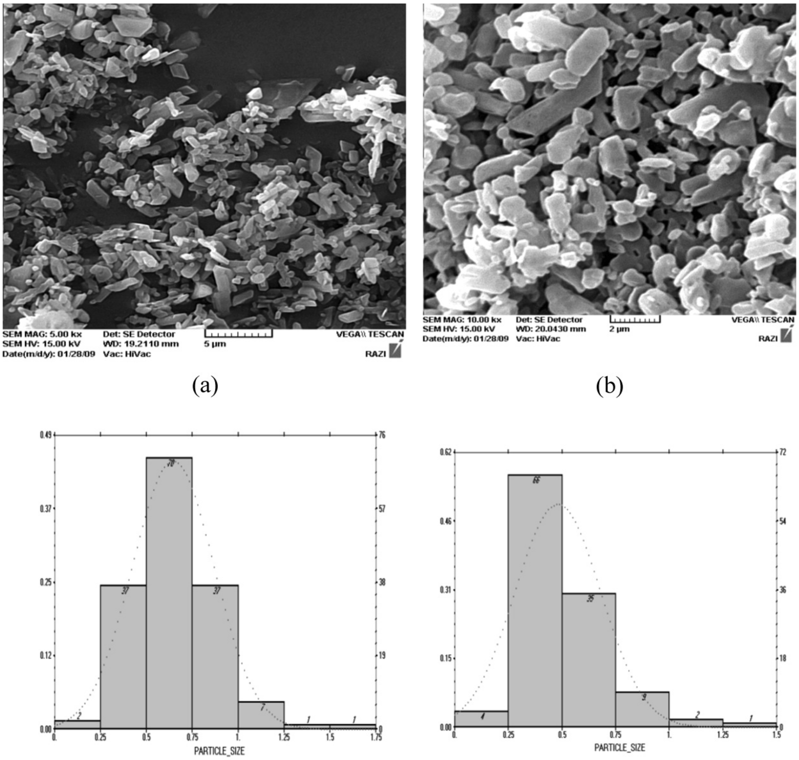


(a) (b)

Figure 3. Effect of surfactant on the scanning electron micrographs of spray to the solution of HMX: (a) HMX prepared in the absence of surfactant and (b) HMX particles prepared by addition of surfactant.

Effect of Slurry Temperature

Another parameter of particle size control can be achieved by varying the slurry temperature. Figure 4 shows the effect of acetone slurry temperature on the particle size of prepared particles. Slurry at 20°C temperature results in HMX particles of



(a) (b)

(c) (d)

Figure 4. Effect of solution temperature on the particle size of prepared HMX: (a) scanning electron micrograph of HMX produced at 50°C, (b) scanning electron micrograph of HMX produced at 20°C, (c) particle size distribution curve for HMX produced at 50°C, and (d) particle size distribution curve for HMX produced at 20°C.

about 617 nm; however, increasing slurry temperature to 50°C under the same conditions causes an increase in particle size to about 847 nm.

Effect of Varying the Inlet Air Flow Rate on Particle Size

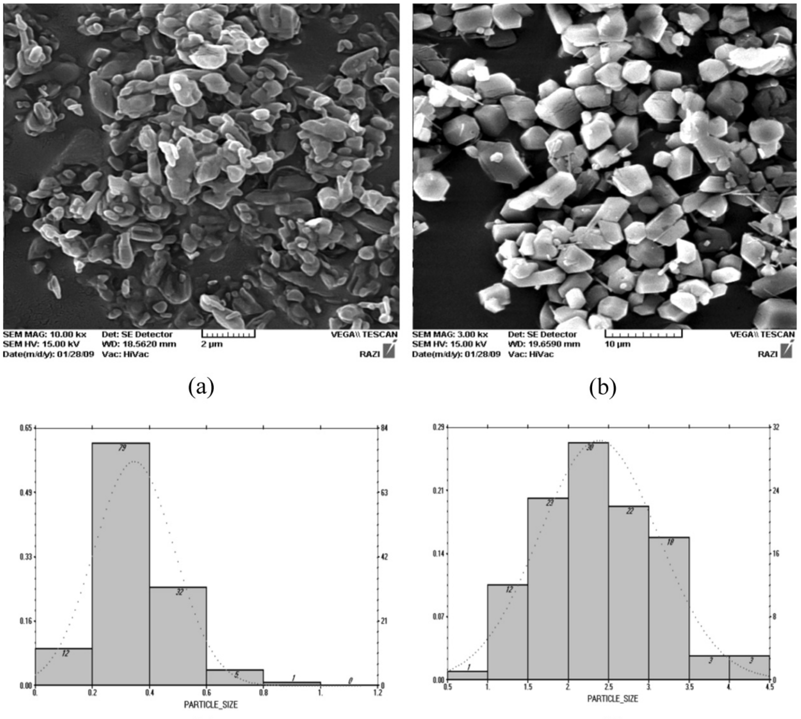
In two of the experiments the inlet air flow rate was varied over a wide range (20–40 L/min) while keeping the other parameters (such as slurry flow rate) approximately constant. The inlet air flow rate was found to have a marked effect on the particle size of the produced HMX, and increased inlet air flow rate from 20 to 40 L/min air flow rate decreased the particle size of HMX from 617 to 481 nm (Table 1). Thus, milder and slower inlet air flow rate produced particles with smaller diameter.

Effect of Varying the Slurry Flow Rate on Particle Size

Another parameter of HMX particle size control is slurry flow rate. Therefore, in three of the experiments the slurry flow rate was varied over a wide range (0.0025–0.012 L/min) while keeping the other parameters constant. The slurry flow rate was found to have a marked effect on the particle size, which decreased from 481 nm at 0.0075 L/min slurry flow rate to 347 nm at 0.0025 L/min slurry flow rate (Table 1). However, the particle size of slurry HMX increased from 347 nm at 0.0025 L/min slurry flow rate to about 2.4 μm at higher air flow rate of 0.012 L/min. Thus, 0.0025 L/min is the optimum slurry flow rate for generation of HMX particles with the lower sizes. Figure 5 shows scanning electron micrographs (SEMs) of HMX particles obtained at various slurry flow rate.

Effect of Anti-Solvent Temperature

Another important practical feature of the method is anti-solvent temperature. A saturated solution of HMX in acetone was spray to water as anti-solvent at two different temperatures to study the effect of anti-solvent temperature.



(a) (b)

(c) (d)

Figure 5. Effect of slurry flow rate on the particle size of prepared HMX: (a) scanning electron micrograph of HMX produced at 0.0025 L/min, (b) scanning electron micrograph of HMX produced at 0.012 L/min, (c) particle size distribution curve for HMX produced at 0.0025 L/min, and (d) particle size distribution curve for HMX produced at 0.012 L/min.

The results showed that the particle size of HMX particles decreased with reduced anti-solvent temperature (Table 1).

Effect of Other Variables on the HMX Particle Properties

The effect of using the two nozzles on the powder particle size of HMX was investigated with increase in size of the nozzles from

0.8 to 1.2 mm; the particle size of the produced HMX was increased from 5 to 10 μm.

Stirring of the anti-solvent during spraying in non-solvent was also an important factor affecting the characteristics of the products. Two experiments were designed in the presence and absence of the anti-solvent, and other operating conditions were equal. The size distribution data showed that the size range was different and particle size decreased with the stirring of the slurry.

Conclusion

The control of submicron particle size prepared by the spraying an acetone solution of HMX non-solvent was investigated experimentally and the results are explained qualitatively. Solvent and anti-solvent temperatures, air flow rate, slurry flow rate, stirring, and addition of reductant interfacial forces play important roles in controlling the particle size of the HMX particles. The results showed that all of above motional variables are crucial parameters that affect the particle size of the prepared particles. The XRD pattern shows that the polymorph of prepared HMX is β (Fig. 1). We also found that the method of spraying in non-solvent permits the control of the particle size and shape by varying the preparation conditions. The results open a new route to controlling the formation of a wide variety of submicron explosive particles.

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